



Mechanism of adsorption of Cu^{2+} and Zn^{2+} on the corn silk (*Zea mays* L.)



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ABSTRACT

In this study the novel biosorbent – raw corn silk (CS) was investigated for Cu^{2+} and Zn^{2+} removal from aqueous solutions. The physical and chemical properties of CS were determined by SEM – EDX and ATR – FTIR techniques. The SEM micrographs revealed that surface morphology of CS is suitable for metal adsorption, while FTIR analysis confirmed presence of various active groups (O–H, C–O, C–O–C, C=C and amide II) which could interact with metal ions. The adsorption experiments were performed in batch system. Experimental data were fitted by pseudo – first order and pseudo – second order kinetic models as well as Langmuir and Freundlich isotherm models. Biosorption of the both metals follow pseudo second-order kinetic model. The best fitting adsorption model is Langmuir model and the maximum biosorption capacities (q_{max}) for Cu^{2+} and Zn^{2+} at 313 K and pH 5.0 were 15.35 mg g^{-1} and 13.98 mg g^{-1} , respectively. The thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were studied at different metal concentration and three temperatures. According to thermodynamic study, the biosorption process for both metals is feasible, endothermic and spontaneous. According to thermodynamic study, the biosorption process for both metals is feasible, endothermic and spontaneous. Ion – exchange is the dominant mechanism in adsorption of Cu^{2+} and Zn^{2+} on the CS with a certain degree of complexation. Desorption study was performed in three adsorption/desorption cycles with diluted nitric acid. Results show that after metal adsorption CS can be efficiently recovered and reused for new adsorption process. Obtained results indicated that corn silk could be used as efficient novel biosorbent for Cu^{2+} and Zn^{2+} removal from water samples.

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1. Introduction

Intensive technological and industrial development, along with the growth of other human activity, has led to excessive use of water resources and increasing water pollution. Consequently, there is less and less clean water. The main sources of water pollution are electroplating, mining and smelting industry, burning of fossil fuels, electronic industry, and many others. These sources contaminate the waters and the wider environment with inorganic waste. This waste is problematic because it contains a high concentration of heavy metals, which are toxic, non-degradable and accumulate in living organisms, thus accumulate in the food chain. High concentration of heavy metals can cause various health problems in humans. This justifies attempts to protect the water from any form

of pollution and to seek most acceptable solutions to protecting the planet.

There are many conventional techniques for treatments of waste water such as membrane filtration, coagulation, chemical precipitation or ion exchange. These methods are limited because of high costs or production of large amounts of secondary waste (for example, sludge after precipitation). Another efficient technology for the removal of heavy metals from drinking and industrial waste waters uses activated carbon. However, the high costs of producing activated carbon, and losses during regeneration, limit its use (Bulut and Tez, 2007; Li et al., 2013; Liao et al., 2011). Adsorption proved to be an efficient method for removal of heavy metals from waste water. In recent years, a lot of research has been carried out on possible use of alternative materials for sorption treatment of polluted waters. Various researchers have investigated metal ion adsorption on raw, immobilised and chemically modified biomass. Most of these papers have shown that immobilised and chemically modified biomaterials have larger sorption capacity than raw

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biomaterials. However, pre-treatment of biomaterials generates a large amount of metal-contaminated wastewater from the modification process (including wastewater from rinsing of modified biosorbent). For that reason, investigations of raw biomaterials are still desirable. A lot of investigations have been done using various agro waste materials such as: hazelnut shell, almond shell (Pehlivan et al., 2009), cashew nut shell (Coelho et al., 2014), apricot stone (Petrović et al., 2015; Šoštarić et al., 2015), date pit (Albadarin et al., 2014), grape stalk waste (Martinez et al., 2006), olive tree pruning (Calero et al., 2013), orange peel (Varshini et al., 2015), wheat straw (Gorgievski et al., 2013), rice bran (Zafar et al., 2015), corn cob (Petrović et al., 2015), sugarcane bagasse (Ullah et al., 2015), agave bagasse (Velazquez-Jiminez et al., 2013), etc. These biomaterials are by-products or waste products from large scale industrial processes, as well as agricultural waste materials. The advantage of heavy metal adsorption on the agro waste materials compared to conventional methods is its low price, high efficiency, minimal chemical and biological sludge and the possibility of regeneration.

Maize is grown in large quantities all over the world. After the harvest a large amount of the plant parts remain on corn fields as crop residue and are available for different agricultural and industrial uses. One of these crop residues with no commercial value or use is corn silk (CS). Previous study (Petrović et al., 2016) has revealed that CS is suitable for adsorption of lead ions from water solutions. The aim of this study is a further and extended research of possible CS usage for copper and zinc removal from water solution, due to fact that both heavy metals are among the most common pollutants found in ground and industrial effluents. These metals tend to bioaccumulate in living organisms, due to their high solubility and mobility they represent a serious ecological and health hazard (Al-Rub et al., 2006).

In this paper, possible use of raw CS as a biosorbent of copper and zinc metal ions from the water solutions was investigated for the first time. Chemical and physical properties of CS, before and after metal adsorption, were investigated using several instrumental techniques. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the functional groups that are involved in binding of copper and zinc to the biomaterial, while Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray analysis (EDX) were used to detect possible changes in CS morphology during adsorption process. In order to define kinetics and adsorption process equilibrium, corresponding kinetic and isotherm models were applied. Also, the paper investigated binding mechanisms of copper and zinc onto CS, as well as the possibility of regeneration and reuse of this biomaterial as biosorbent.

2. Materials and methods

2.1. Preparation of the CS and metal solution

CS was obtained from the planted corn near Belgrade (Serbia). Samples were washed with deionized water to remove impurities from its surface and dried at 353 K. After that the CS was ground and sieved to obtain <0.2 mm particles. The CS was then dried until constant weight, stored and used as such without any pretreatment.

The stock solution of Cu^{2+} and Zn^{2+} (0.1 mol L^{-1}) was prepared by dissolving a precise amount of $\text{Cu}(\text{NO}_3)_2 \times 3 \text{ H}_2\text{O}$ and $\text{ZnSO}_4 \times 7 \text{ H}_2\text{O}$ (p.a. grade), respectively in deionized water. The experimental metal solutions from 5 to 240 mg L^{-1} were prepared by dilutions of stock solution with deionized water.

2.2. Characterization of the CS

Dried samples were dissolved using the nitric-perchloric acid digestion method (Hseu, 2004) and inorganics (K, Na, Mg, Ca,

Cd, Cu, Zn, Ni, Pb, Fe, Al, Mn) were determined from the solution by Atomic Absorption Spectrophotometry (AAS) using Perkin Elmer AAAnalyst 300 Spectrophotometer. For determination of metal ion concentration in solutions, calibration curves prepared from certified standard stock solutions of corresponding metal ions were used. Determination of phosphorus was performed from acid digested sample solutions using UV-vis spectroscopy (Jena Analytic, Spekol1300) (Awwad et al., 2013). Ash and moisture content of the CS were determined according to standard methods ASTM E871-82 (2013) and ASTM E1755-01 (2015). The elemental analysis (C, H, N and S) of the CS was performed on VARIO-EL III CHNS-O Analyser (Elementar – Hanau, Germany). Operating ranges were: 0.03–20 mg for C; 0.03–3 mg for H; 0.03–2 mg for N and 0.03–6 mg for S. Oxygen content was calculated by subtracting the sum of all obtained elemental values from 100%.

The point of zero charge, specific surface area and pore volume of CS was determined as described elsewhere (Milonjić et al., 1975; Petrović et al., 2016).

Scanning Electron Microscopy and Energy Dispersive X-Ray analysis (SEM – EDX) was used to analyse the morphology of CS before and after metal adsorption. Dried CS samples were coated with thin layer of gold. Prepared samples were put under vacuum and then scanned using a JEOL JSM-6610 LV SEM model.

Attenuated Total Fourier Transform Infrared Spectroscopy (ATR – FTIR) was used to determine functional groups which are involved in Cu^{2+} and Zn^{2+} adsorption on the CS. Dried CS samples were analysed using Thermo Nicolet 6700 FT-IR in the spectral range $4000\text{--}400 \text{ cm}^{-1}$ with 32 scans and resolution of 4 cm^{-1} .

2.3. Adsorption study

Batch adsorption experiments were conducted in 100 mL Erlenmeyer flasks containing 0.5 g of CS and 50 mL of each metal solution at initial pH 5.0. Biosorption experiments for each metal were investigated separately under the same operating conditions: contact time (2–180 min), initial metal concentration ($5\text{--}240 \text{ mg L}^{-1}$) and temperature (293–313 K). The biosorption capacity of Cu^{2+} and Zn^{2+} increased with an increase of pH value of the solution. With an increase of the pH value, the amount of OH^- ions in the solution increases and they can react with metal ions to form hydrolysis products, which may have negative influence on the biosorption process of M^{2+} . Previous studies (Doyle and Liu, 2003; Smičiklas, 2007; Regmi et al., 2012) have shown that aqueous metal solutions have to be kept at $\text{pH} < 5.5$ so that copper and zinc ions are present in Cu^{2+} and Zn^{2+} ionic forms. Similarly, in this study precipitation of copper and zinc hydroxides was observed at $\text{pH} > 5.0$ (Fig. S1). In order to avoid hydrolysis and precipitation of metal hydroxides, all experiments were carried out at initial pH 5.0. The initial pH value of metal solution was adjusted by adding small amounts of $0.01 \text{ mol L}^{-1} \text{ HNO}_3$ and $0.01 \text{ mol L}^{-1} \text{ KOH}$ and measured using pH meter (Senslon MM340). The suspensions were shaken in a mechanical shaker at 250 rpm. At the end of the experiments, the suspensions were filtered and the concentration of Cu^{2+} and Zn^{2+} was determined by AAS. All adsorption experiments were performed in triplicate.

The adsorption capacity of Cu^{2+} and Zn^{2+} on the CS was evaluated from the following equation:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where q_e is the amount of Cu^{2+} and Zn^{2+} adsorbed on the CS (mg g^{-1}), C_0 and C_e are the initial and equilibrium Cu^{2+} and Zn^{2+} concentrations in solution (mg L^{-1}), V is the volume of metal solution (L) and m is the mass of the CS (g).

The experimental data were evaluated by Langmuir and Freundlich isotherm models as well as pseudo – first order and pseudo – second order kinetic models.

2.4. Ion exchange mechanism

To investigate ion exchange mechanism the CS was shaken for 120 min (250 rpm) with metal solution of different concentration (5–120 mg L⁻¹). Then, suspensions were filtered and concentration of Cu²⁺, Zn²⁺, K⁺, Na⁺, Mg²⁺ and Ca²⁺ was measured by AAS. Concentrations of released ions (K⁺, Na⁺, Mg²⁺, Ca²⁺ and H⁺) from the control sample (CS and deionized water) were also measured. The pH value of each solution was measured using pH – meter and the concentration of H⁺ was calculated using following equation:

$$[H^+] = 10^{pH_f} - 10^{pH_i} \quad (2)$$

where [H⁺] concentration of H⁺ released, pH_i and pH_f are the pH value of metal solution before and after adsorption, respectively.

2.5. Desorption study

The CS (1.0 g L⁻¹) was shaken with 40 mg L⁻¹ metal solution for 120 min at room temperature and pH 5.0. After that, suspensions were filtered and rinsed with deionized water to remove non – absorbed metal ions. Then, metal loaded CS was added to different eluents such as: deionized water at initial pH of 4.0 and 2.0 and 0.1 mol L⁻¹ HNO₃ and shaken for 120 min at room temperature. The pH value of water solutions were adjusted by adding small amounts of HNO₃. The suspensions were filtered through a filter paper, rinsed several times with deionized water and dried at 353 K. The adsorption – desorption experiments with 0.1 mol L⁻¹ HNO₃ were repeated in three cycles. The concentration of Cu²⁺ and Zn²⁺ in supernatants was analyzed by AAS. Desorption efficiency was computed by the Eq. (3):

$$d_E = (q_d/q_a) \times 100 \quad (3)$$

where d_E is desorption efficiency (%), q_d is amount of Cu²⁺ and Zn²⁺ desorbed (mg g⁻¹) and q_a is adsorption capacity of Cu²⁺ and Zn²⁺ adsorbed on the CS (mg g⁻¹).

3. Result and discussion

3.1. Characterization of the CS

The physical and chemical properties of the CS are listed in Table 1.

The SEM micrographs and EDX spectrums of the CS before and after metal adsorption are given in Fig. 1. The CS has a low microporosity (Table 1) but its surface has a large number of micron size channels (Fig. 1 (A)) (Petrović et al., 2016; Zhu et al., 2013). Therefore, nano pores do not play significant role in biosorption of Cu²⁺ and Zn²⁺ on CS. However, micron size channels allow the diffusion of Cu²⁺ and Zn²⁺ ions through the material, and thus, the metal ion adsorption can occur on the interior and exterior of the CS (Garcia-Rosales and Colín-Cruz, 2010). Surface morphology like this is suitable for metal adsorption due to a larger number of active sites. Although, SEM micrographs (Fig. 1(B, C)) revealed no evident physical changes on biosorbent surface after copper and zinc adsorption, EDX spectrums showed the presence of these metal ions on the surface of CS (Fig. 1(D–F)). As can be seen from Fig. 1(D) the EDX spectrum of raw CS shows high content of Ca, K, Mg and P, which also confirmed by the results from the chemical analysis of CS (Table 1). After metal adsorption the Ca, Mg and K peaks reduced and new peaks for Cu²⁺ and Zn²⁺ were observed (Fig. 1(E, F)) suggesting that Cu²⁺ and Zn²⁺ were bound to the CS over the ion exchange mechanism with Ca²⁺, Mg²⁺ and K⁺. Similar considerations were reported in previous investigations for Pb²⁺ removal by *Myriophyllum spicatum* and its compost (Milojković et al., 2014).

Table 1

Physical and chemical properties of the CS.

Parameter	Value
Elemental analysis (%)	
C	45.88
H	6.51
O	43.96
N	3.13
S	0.52
Moisture contents (%)	5.94
Ash contents (%)	4.62
pH	6.15
pH _{pzc}	6.0 [*]
Specific surface area (m ² g ⁻¹)	1.357 [*]
Total pore volume (cm ³ g ⁻¹)	0.002446
Mesopore volume (cm ³ g ⁻¹)	0.002164
Mean mesopore diameter (nm)	6.5056 [*]
Mineral composition (%)	
K	1.587
Na	0.00505
Mg	0.175
Ca	0.122
Cd	0.000375
Cu	0.00075
Zn	0.003524
Ni	0.00025
Pb	0.0001
Fe	0.04849
Al	0.097
Mn	0.00245
P	0.201

^{*} Petrović et al. (2016).

The unmarked peaks at 1.7, 9.7 and 11.5 keV occurred from Au (Fig. 1(D–F)).

In order to analyze the functional groups, which are responsible for adsorption of Cu²⁺ and Zn²⁺ on the CS the FTIR spectrums before and after metal adsorption were done in the range 4000–400 cm⁻¹. The FTIR spectrums are given in Fig. 2. As shown, numerous peaks are present suggesting complex nature of the CS. The FTIR spectral analysis of raw CS was interpreted to the details in our previous investigation (Petrović et al., 2016). The functional groups observed in the FTIR spectrums of raw CS and CS after metal adsorption are listed in Table 2.

Because of interaction between functional groups and metal loaded on the adsorbent, the intensity as well as the position of the FTIR peaks were changed (Wang et al., 2015). As can be seen (Fig. 2) the intensity of all peaks at FTIR spectra decreased after Cu²⁺ and Zn²⁺ adsorption on the CS. In addition, some of peaks shifted to lower or higher wavenumbers (Table 2). The peak intensity of the –OH stretching vibration significantly decreased and shifted from 3285 to 3293 and 3296 cm⁻¹ after Cu²⁺ and Zn²⁺ adsorption, respectively, suggesting the possible formation of complexes between –OH groups and metal loaded (Chen et al., 2010; Petrović et al., 2016). The peak intensity of the peaks at 1546, 1420, 1376, 1250 and 1150 cm⁻¹ decreased and the wavenumber was shifted indicated that amide II, C=C, –OH and –C –O bands are involved in Cu²⁺ and Zn²⁺ adsorption on the CS. The results of FTIR analysis suggest that the complexation process is involved in the adsorption of Cu²⁺ and Zn²⁺ on the CS, which is also confirmed by the kinetic study.

3.2. Kinetic study

All kinetics experiments were performed at three temperatures (293, 303 and 313 K) and for three Cu²⁺ and Zn²⁺ concentrations (10, 20 and 40 mg L⁻¹) at different contact times (2 to 120 min). In this work the pseudo – first order and pseudo – second order models were used for fitting kinetic experimental data and can be

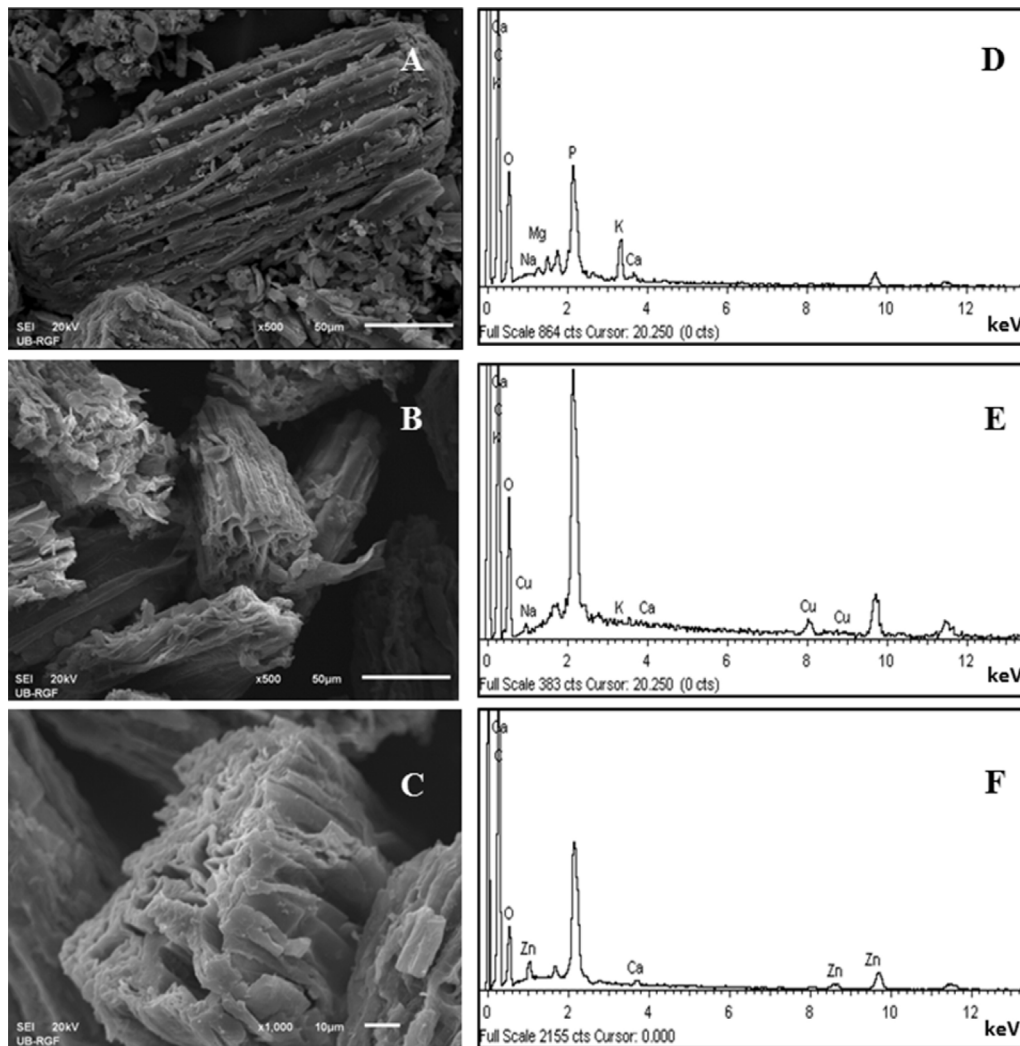


Fig. 1. SEM micrographs of the raw CS (A); CS after Cu²⁺ adsorption (B) and CS after Zn²⁺ adsorption (C). EDX spectrums of the raw CS (D); CS after Cu²⁺ adsorption (E) and CS after Zn²⁺ adsorption (F).

Table 2
Peak positions in the FTIR spectrums of raw CS and after Cu²⁺ and Zn²⁺ adsorption.

Wavenumber (cm ⁻¹)			Assignment	Refs.
raw CS	Cu ²⁺ – CS	Zn ²⁺ – CS		
3285	3293	3296	—OH stretching	Tong et al., 2011
2918	2918	2917	—CH stretching	Pujol et al., 2013
2850	2850	2850	—CH stretching	Pujol et al., 2013
1733	1733	1733	C=O	Tong et al., 2011; Lyman et al., 2003
1637	1637	1637	C=O stretching	Jacques et al., 2007; Pavia et al., 1996
1546	1541	1537	Amide II band	Yee et al., 2004
1420	1437	1432	C=C stretching	Martinez et al., 2006; Pehlivan et al., 2009
1376	1370	1370	—OH bending/CH ₃ deformation	Chen et al., 2010
1250	1247	1243	—C—O stretching	Akar et al., 2013
1150	1154	1154	—C—O—C stretching	Akar et al., 2013
1032	1032	1032	—C—O/—C—N	Blázquez et al., 2011

expressed as Eqs. (4) and (5), respectively (Ho and Mckay, 1999; Lagergren, 1898):

$$1/q_t = 1/q_e + k_1/q_e t \quad (4)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (5)$$

where k_1 and k_2 is the pseudo – first order and pseudo – second order rate constant (min⁻¹), respectively. The k_1 and q_e can be determined from the slope and intercept of the linear plot of $1/q_t$

versus $1/t$ and the k_2 and q_e can be calculated from the slope and intercept of the linear plot of t/q_t versus t . Experimental data for the pseudo – first order and pseudo – second order kinetic models are given in Fig. S2 and S3, respectively.

The obtained parameters of kinetic models are summarized in Table 3. The calculated values of q_e ($q_{e,cal}$) are very close to experimental values. The values of R^2 of the pseudo – second order model are closer to unity than of the pseudo-first-order model. This indicates that the metal adsorption on the CS can be described by the

Table 3
Kinetic parameters for the Cu²⁺ and Zn²⁺ adsorption on the CS.

Metal	Temperature (K)	293			303			313		
		Concentration (mg L ⁻¹)			Concentration (mg L ⁻¹)			Concentration (mg L ⁻¹)		
Cu	$q_{e,exp}$ (mg g ⁻¹)	8.47	9.20	12.50	8.55	9.65	14.20	8.61	10.40	16.10
	Pseudo – first order model									
	$q_{e,cal}$ (mg g ⁻¹)	8.46	8.95	12.47	8.51	9.64	13.94	8.57	10.42	15.74
	k_1 (min ⁻¹)	1.454	0.918	0.722	1.309	0.806	0.623	1.119	0.639	0.612
	R^2	0.983	0.966	0.983	0.976	0.979	0.952	0.967	0.969	0.936
	Pseudo – second order model									
Zn	$q_{e,cal}$ (mg g ⁻¹)	8.61	9.31	12.62	8.68	9.74	14.34	8.73	10.5	16.27
	k_2 (g mg ⁻¹ min ⁻¹)	0.072	0.062	0.091	0.076	0.115	0.062	0.091	0.141	0.05
	R^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	$q_{e,exp}$ (mg g ⁻¹)	6.05	8.50	11.10	6.30	9.10	11.60	6.62	9.40	12.70
	Pseudo – first order model									
	$q_{e,cal}$ (mg g ⁻¹)	6.20	8.66	11.18	6.42	9.14	11.73	6.75	9.60	12.65
	k_1 (min ⁻¹)	1.073	0.922	0.761	0.929	0.848	0.709	0.948	0.783	0.755
	R^2	0.980	0.996	0.946	0.977	0.991	0.937	0.984	0.994	0.955
	Pseudo – second order model									
	$q_{e,cal}$ (mg g ⁻¹)	6.12	8.55	11.25	6.33	8.95	11.83	6.66	9.53	12.68
	k_2 (g mg ⁻¹ min ⁻¹)	0.241	0.176	0.110	0.285	0.339	0.117	0.252	0.165	0.119
	R^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999

Table 4
Langmuir and Freundlich isotherm parameters for adsorption of Cu²⁺ and Zn²⁺ on the CS.

Metal	T (K)	Langmuir isotherm model				Freundlich isotherm model		
		q_{max} (mg g ⁻¹)	K_L (L mg ⁻¹)	R_L	R^2	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R^2
Cu	293	12.67	1.062	0.0039	0.956	7.319	8.06	0.792
	303	14.42	0.853	0.0049	0.962	7.746	7.14	0.821
	313	15.35	0.924	0.0045	0.881	8.085	6.33	0.853
Zn	293	11.14	0.912	0.0045	0.968	6.364	7.93	0.817
	303	12.56	0.702	0.0059	0.969	6.494	6.80	0.838
	313	13.98	0.999	0.0042	0.984	7.958	7.90	0.767

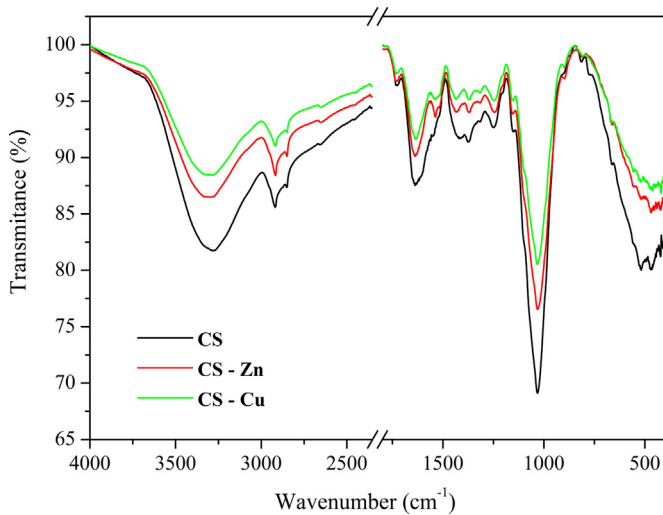


Fig. 2. The FTIR spectrums of raw CS and CS after Cu²⁺ and Zn²⁺ adsorption.

pseudo – second order model which means that the complexation and ion exchange mechanism are involved in adsorption of Cu²⁺ and Zn²⁺ on the CS (OuYang et al., 2014; Padmavathy et al., 2003; Zhong et al., 2012). This is in agreement with the results of EDX and FTIR analysis and ion exchange mechanism study.

3.3. Adsorption isotherm study

Equilibrium experiments were performed for different Cu²⁺ and Zn²⁺ concentrations (5–240 mg L⁻¹) at different temperatures (293, 303 and 313 K) for 120 min at pH 5.0. In order to investigate the

adsorption equilibrium between the metal ion in solution and CS, the experimental data were analyzed with the Langmuir and Freundlich isotherm models using Eqs. (6) and (7), respectively (Langmuir, 1918; Freundlich, 1906):

$$q_e = q_{max} K_L C_e / (1 + K_L C_e) \quad (6)$$

$$q_e = K_F C_e^{1/n} \quad (7)$$

where q_{max} is the maximum amount of metal adsorbed on the adsorbent (mg g⁻¹), K_L is the Langmuir constant (L mg⁻¹) and K_F is the equilibrium constant and $1/n$ is an empirical parameter. The q_{max} and K_L can be determined from the slope and intercept of the non-linear plot of q_e versus C_e . The K_F and $1/n$ can be determined from the slope and intercept of the non-linear plot of q_e versus C_e . The n values were evaluated at different temperatures.

R_L is the dimensionless constant, which can be used to describe feasibility of Langmuir isotherm model and favorability of adsorption process (Weber and Chakravorti, 1974). It is expressed as the following equation:

$$R_L = 1 / (1 + K_L C_0) \quad (8)$$

where C_0 is the highest initial metal concentration (mg L⁻¹).

Experimental data for Langmuir and Freundlich isotherm models are given in Fig. S4. The calculated parameters of Langmuir and Freundlich isotherm models for Cu²⁺ and Zn²⁺ adsorption on the CS at different temperatures are summarized in Table 4.

It was revealed, due to the higher value of correlation coefficient R^2 that the Langmuir isotherm model fits better with the experimental data than the Freundlich isotherm model. Commonly, the Langmuir isotherm model better describes adsorption on homogeneous surfaces, while the Freundlich isotherm model is better for heterogeneous surfaces (Langmuir, 1918; Xue et al., 2012). Thus, the model results suggest that the bonding of Cu²⁺ and Zn²⁺ occurs

Table 5

The maximum biosorptive capacities for Cu^{2+} and Zn^{2+} removal from aqueous solutions of different agro waste materials.

Agro waste material (modification type)	q_{max} (mg g^{-1})		Refs.
	Cu	Zn	
Corn cob (raw)	3.40		Petrović et al. (2015)
Apricot stone (raw)	5.90		Petrović et al. (2015)
Rice straw (raw)	5.00	3.25	Gorgievski et al. (2013)
Rice straw (HNO_3 -NaOH)	8.13	8.63	Rocha et al. (2009)
Rice husk (alkali treated)		8.14	Krishnani et al. (2008)
Agave bagasse (raw)		7.84	Velazquez-Jimenez et al. (2013)
Agave bagasse (HNO_3)		12.4	Velazquez-Jimenez et al. (2013)
Agave bagasse (NaOH)		20.24	Velazquez-Jimenez et al. (2013)
Sawdust (raw)	2.54	0.98	Šćiban et al. (2006)
Sawdust (NaOH)	6.92	15.8	Šćiban et al. (2006)
Corn silk (raw)	15.35	13.98	This work

under monolayer adsorption on the homogeneous surface (Chen et al., 2010). Table 4 demonstrates that the n and R_L values are between 0 and 10 and 0–1, respectively, which serves to indicate favorable adsorption of Cu^{2+} and Zn^{2+} on the CS (Hanif et al., 2007).

The maximum adsorption capacity of Cu^{2+} and Zn^{2+} on the CS reaches values of 15.35 and 13.98 mg L^{-1} , respectively (Table 4). When put against other investigated raw and treated agro – waste materials (Table 5), it can clearly be seen that CS has a good adsorptive characteristics. These results demonstrate that CS can be successfully used as an adsorbent of copper and zinc removal from aqueous solution even without any modifications.

3.4. Thermodynamic study

The Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) values were studied for three different Cu^{2+} and Zn^{2+} concentration (10, 20 and 40 mg L^{-1}) at three different temperatures (293, 303 and 313 K) and computed using the following equations:

$$\Delta G = -RT \ln K_d \quad (9)$$

$$\Delta G = \Delta H - T \Delta S \quad (10)$$

$$\ln K_d = -\Delta H/RT + \Delta S/R \quad (11)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is absolute solution temperature (K) and K_d (q_e/C_e) is the distribution coefficient. The values of ΔH and ΔS were obtained from the slope and intercept of the plot of $\ln K_d$ versus $1/T$.

The calculated thermodynamic parameters are listed in Table 6. The negative values of ΔG indicated feasibility and spontaneous nature of the Cu^{2+} and Zn^{2+} adsorption on the CS. The adsorption process is more energetically favorable at higher temperatures and lower concentrations due to value of ΔG , which decreases with the increasing of temperature, as well as increases with increasing of metal concentrations (Asem et al., 2008; Saha and Chowdhury, 2011; Sevim et al., 2011; Wang et al., 2010). The positive ΔH values indicate that the adsorption process of Cu^{2+} and Zn^{2+} on the CS is endothermic in nature. The positive ΔS values implied the increased randomness at the solid/liquid interface during Cu^{2+} and Zn^{2+} adsorption on the CS (Malkoc and Nuhoglu, 2007).

3.5. Ion – exchange mechanism

The ion – exchange mechanism is defined as equal replacement of ion in solid phase by the ion in solution (Kragović et al., 2012). In order to investigate the involvement of ion – exchange mechanism in the adsorption of Cu^{2+} and Zn^{2+} on the CS, displacement of Ca^{2+} , Mg^{2+} , K^+ , Na^+ and H^+ was investigated. The amounts of

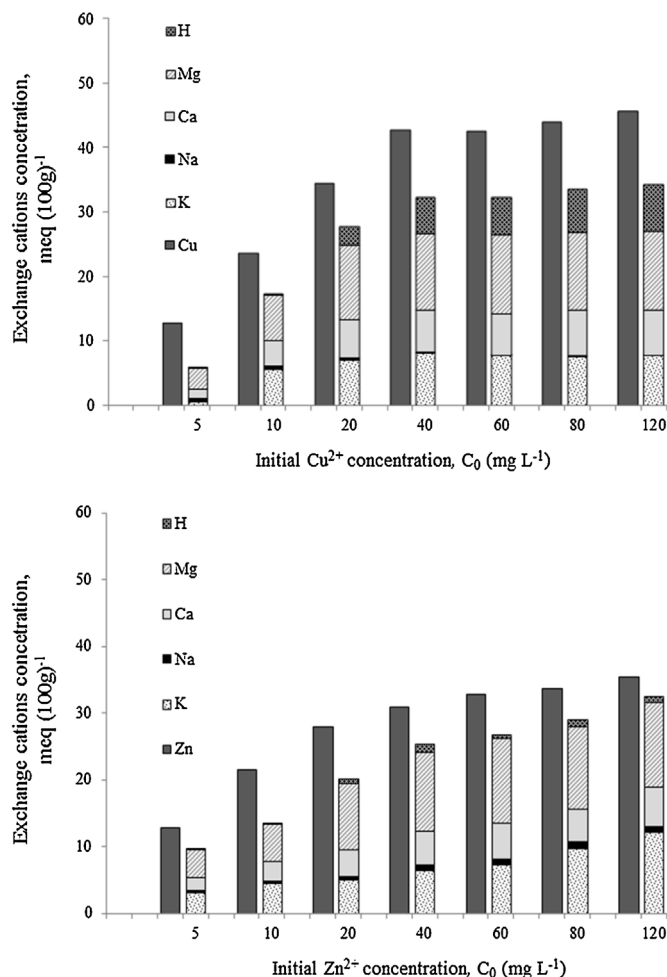


Fig. 3. The amounts of Cu^{2+} (A) and Zn^{2+} (B) adsorbed and amounts of Ca^{2+} , Mg^{2+} , K^+ , Na^+ and H^+ displaced at different metal initial concentrations.

metal adsorbed and the amount of cations displaced from the CS at different metal ion concentrations (5–120 mg L^{-1}) are shown in Fig. 3. As can be seen, uptake of Cu^{2+} and Zn^{2+} on the CS increased with increasing metal concentrations from 5 to 40 mg L^{-1} afterward there no visible change in the metal uptake. At the other hand, displacement of the Ca^{2+} , Mg^{2+} , K^+ , Na^+ and H^+ by metal adsorption was increased with increasing metal concentration. Also, decrease of pH value of metal solution during biosorption process of Cu^{2+} and Zn^{2+} onto CS was observed. It indicates that H^+ ions were released from the CS to solution which confirms previous allegations. Based on the results (Fig. 3), it is clear that the Cu^{2+} and Zn^{2+} is mostly exchanged with K^+ and Mg^{2+} ions. According to previous investigations it can be concluded that replacement of the Ca^{2+} , Mg^{2+} , K^+ and Na^+ by metal indicates ionic bonding while replacement of H^+ by metal indicates covalent bonding of the Cu^{2+} and Zn^{2+} on the CS (Avery and Tobin, 1993; Crist et al., 1990; Šćiban et al., 2006).

The amount of Ca^{2+} , Mg^{2+} , K^+ , Na^+ and H^+ displaced is not equal to the amount of Cu^{2+} and Zn^{2+} adsorbed (Fig. 3). The amount of cations displaced from the CS is lesser than the amount of metal adsorbed. It indicates that some other binding mechanisms, except ion – exchange mechanism, are involved in Cu^{2+} and Zn^{2+} adsorption on the CS (Šćiban et al., 2006). Involvement of ion – exchange mechanism was also confirmed with EDX analyses while complexation process was confirmed with ATR – FTIR analysis and kinetic study.

Table 6Thermodynamic parameters for Cu²⁺ and Zn²⁺ adsorption on the CS.

Metal	Concentration (mg L ⁻¹)	ΔG (kJ mol ⁻¹) at T (K)			ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
		293	303	313		
Cu	10	-21.42	-22.32	-23.22	5.09	90.19
	20	-17.10	-18.06	-19.01	10.75	95.08
	40	-14.91	-15.93	-16.95	15.01	102.10
Zn	10	-17.94	-18.88	-19.82	9.59	93.95
	20	-16.68	-17.52	-18.36	7.83	83.68
	40	-14.52	-15.27	-16.00	7.32	74.53

3.6. Desorption study

In order to investigate possibility of recycling the CS and recovery of the copper and zinc, desorption study was carried out. Metal loaded CS was treated with three different solutions: 0.1 mol L⁻¹ HNO₃, deionized water at pH 2.0 and deionized water at pH 4.0. It was found that desorption efficiency was 92.96% Cu in 0.1 mol L⁻¹ HNO₃, 92.80% Cu in deionized water at pH 2.0 and 5.36% Cu in deionized water at pH 4.0. On the other hand, desorption efficiency was 99.0, 91.60 and 2.52% for Zn, in 0.1 mol L⁻¹ HNO₃, deionized water at pH 2.0 and deionized water at pH 4.0, respectively. The desorption study showed that almost all adsorbed metal ions were recovered in acid solution. However, desorption efficiency of both metals are lower than 6.0% at pH 4.0, which indicates that coordination complexes between metal ions and active functional groups could be of inner-sphere (Velazquez-jiminez et al., 2013).

The adsorption – desorption experiments were performed with 0.1 mol L⁻¹ of HNO₃. The desorption efficiency through three cycles was more than 87.7 and 73.4% for Cu²⁺ and Zn²⁺, respectively. It can be concluded that CS after metal adsorption can be efficiently recovered and reused for new adsorption process. The adsorption capacity decreased from 14.9 to 7.7 and from 11.9 to 8.2 mg g⁻¹ for Cu²⁺ and Zn²⁺, respectively through three adsorption – desorption cycles. The lesser adsorption capacity after various adsorption – desorption cycles indicates that the Cu²⁺ and Zn²⁺ adsorption on the CS is partially recoverable process (Petrović et al., 2016).

4. Conclusion

In this study, for the first time, the usefulness of raw CS as adsorbent for Cu²⁺ and Zn²⁺ removal from aqueous solutions was investigated.

Experimental data for Cu²⁺ and Zn²⁺ adsorption on the CS were best fitted to pseudo – second order kinetic model indicating involvement of complexation and ion – exchange binding mechanism. Equilibrium data best fitted to Langmuir isotherm model suggesting monolayer adsorption of Cu²⁺ and Zn²⁺ on the CS. The calculated values of Gibbs free energy charge (ΔG) indicates feasible and spontaneous nature of adsorption process, which is energetically favorable at higher temperatures and lower metal concentration. The positive values of enthalpy change (ΔH) indicate endothermic nature of adsorption process.

The CS could be successfully regenerated with diluted nitric acid and reused for new adsorption processes. Summarizing results from this study (EDX and FTIR spectrums before and after metal adsorption, ion – exchange study and kinetic study) it can be concluded that the whole process of Cu²⁺ and Zn²⁺ adsorption on the CS was predominated by ion – exchange mechanism, followed by a certain degree of surface complexation. The most significant cations involved in ion-exchange during Cu²⁺ biosorption are Mg²⁺, K⁺ and H⁺, respectively, while Zn²⁺ is mainly exchanged with Mg²⁺ and K⁺ during adsorption on the CS. It suggests that covalent and ionic bonds are formed between Cu²⁺ and Zn²⁺ ions and active groups on the CS during biosorption process. At the basis on desorption study

it can be concluded that adsorption process of Cu²⁺ and Zn²⁺ on the CS is partially recoverable. The formation of coordination complexes between Cu²⁺ and Zn²⁺ and functional groups on the CS may possibly exist of inner sphere.

The results of this study shows that the raw CS can be used as low cost and efficient adsorbent for Cu²⁺ and Zn²⁺ removal from aqueous solutions due to its high adsorption capacity and reusability.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ecoleng.2016.11.057>.

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